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INVESTIGATIONS OF SURFACE PROPERTIES  
OF SILICON AND OTHER SEMICONDUCTORS

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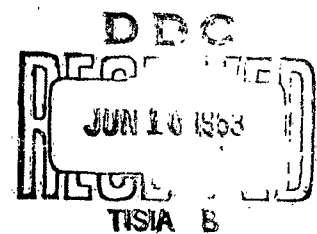
Supplement to the Final Report

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30 September 1962 - 31 January 1963

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ELECTRONICS RESEARCH DIRECTORATE  
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES  
OFFICE OF AEROSPACE RESEARCH  
UNITED STATES AIR FORCE  
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<p>Air Force Cambridge Research Laboratories, Office of Aerospace Research, Bedford, Mass., Rpt. No. AFRL-62-949-(Supplement). WORK FUNCTION AND OXYGEN ADSORPTION PROPERTIES OF NIOBIUM CRYSTALS. Supplement of Final Scientific Rpt, Feb 63, 32p. incl. illus. Unclassified Report</p> <p>This report describes the measurements of photo- electric work functions and oxygen adsorption properties of atomically clean niobium single crystals.</p>	<p>Air Force Cambridge Research Laboratories, Office of Aerospace Research, Bedford, Mass., Rpt. No. AFRL-62-949-(Supplement). WORK FUNCTION AND OXYGEN ADSORPTION PROPERTIES OF NIOBIUM CRYSTALS. Supplement of Final Scientific Rpt, Feb 63, 32p. incl. illus. Unclassified Report</p> <p>This report describes the measurements of photo- electric work functions and oxygen adsorption properties of atomically clean niobium single crystals.</p>	<p>UNCLASSIFIED</p> <p>1. Photoelectric work function</p> <p>1. A F S C Project 5620-Task 56206 Contract AF 19 (604)-5986</p> <p>3. Brown U., Prov., R.I. Supervisors - J. A. Dillon, Jr. and R. M. Oman</p> <p>5. Secondary Rpt No. 62-949 (Supplement) 6. In Astia Collection</p> <p>UNCLASSIFIED</p>	<p>UNCLASSIFIED</p> <p>1. Photoelectric work function</p> <p>1. A F S C Project 5620-Task 56206 Contract AF 19 (604)-5986</p> <p>3. Brown U., Prov., R.I. Supervisors - J. A. Dillon, Jr. and R. M. Oman</p> <p>5. Secondary Rpt No. 62-949 (Supplement) 6. In Astia Collection</p> <p>UNCLASSIFIED</p>
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# ABSTRACT

The photoelectric work functions of atomically clean surfaces of three planes of niobium as measured by the Fowler method are; (111), 4.66; (335), 4.55; (110), 4.33 ev. The work function of ion bombarded surfaces of all three planes is 4.09 ev. The sticking coefficient for oxygen on the clean surfaces is 0.9 and on the ion bombarded surfaces is 0.2. The sticking coefficient for carbon monoxide on these surfaces was found to be at least an order of magnitude lower than the values quoted for oxygen. The work function of ion bombarded surfaces is found to be dependent on the extent of bombardment for bombardments of less than one minute carried out at 0.20 ma/cm<sup>2</sup>. A work function of about 4.7 ev has been observed for a bombardment of 20 seconds on the (335) face. Ion-bombardment etching effects observed on the three planes are similar to those observed on germanium and silicon.

# WORK FUNCTION AND OXYGEN ADSORPTION PROPERTIES OF NIOBIUM CRYSTALS

## I. Introduction

Niobium, the sister element to tantalum, has been used in rather small quantities mainly as an alloying ingredient to produce exceptional mechanical or high temperature properties in industrial metals. Recently there has been some purely scientific interest in niobium because of its exceptional gettering properties (the ability to absorb active gases) and low temperature properties (the superconducting transition temperature is 9.25°K). Element 41 or niobium has atomic mass 92.91, and a melting point of about 2500°C.

There are two rather complete review articles which discuss work function measurements and their interpretations.<sup>1,2</sup> An article by Michaelson<sup>1</sup> summarizes the then (1950) known values of the work functions of the elements, and attempts to correlate the periodic variation of the work functions with the positions of the elements in the periodic table. Other physical properties (first ionization potential and standard electrode potential) which show a periodicity with atomic number are also considered. An article by Herring and Nichols<sup>2</sup> discusses the theoretical problem of calculating the work function and the variation of the work function with crystalline orientation. Both of these articles are hampered by a lack of reliable values of work functions. Niobium is a good example. The work function of niobium wire has been measured thermionically.<sup>3,4</sup> These measurements, apparently made under the best conditions available at that time, suffer from several drawbacks. The measurements were made on wire, and the crystalline planes involved were not known. In each case the cleaning method was to heat in as good a vacuum as possible for long times. In the light of recent work on silicon surfaces and work reported in this article, it appears that the technique of heating the niobium wire immediately after bake out, employed by these experimenters, resulted in considerable surface contamination prior to attempted cleaning.<sup>5,7</sup> This does not mean that these values should be discarded but rather it should be emphasized that the measurements were made on wire outgassed for long times under rather poor vacuum conditions.

Studies of the adsorption properties of niobium are confined almost entirely to high pressure experiments in which there was no attempt to prepare a clean surface.<sup>8,9</sup> A study of the adsorption of CO, CO<sub>2</sub>, and N<sub>2</sub> on niobium films gives some information on multilayer adsorption.<sup>10</sup>



The measurement of the clean surface work function of niobium is therefore by itself of intrinsic value as is the variation of the work function with crystalline orientation. The adsorption of oxygen was studied because of the known gettering properties of niobium and in this case it was found that the oxygen adsorption properties could be used as a measure of the surface condition.

In this work, clean surfaces were prepared using the ion bombardment and annealing method of cleaning. Work function measurements were made on the (111), (110) and (335) planes of niobium crystals both on the clean and ion bombarded surfaces. The adsorption characteristics of the clean and ion bombarded surfaces were also studied. In addition to this work, which was the primary object of the research, it was observed that the work function of ion bombarded surfaces depended on the extent of bombardment for bombardments of less than one minute carried out at  $0.20 \text{ ma/cm}^2$ . This effect, which has not been observed before, could have far reaching consequences for those researchers who prepare surfaces by short bombardments and heatings or by short bombardments alone.<sup>11,12</sup>

## II. Experimental Apparatus and Conditions

The experimental apparatus used in this experiment is similar to that used by others in studying photoelectric properties of metals and semiconductors.<sup>13,14</sup> The crystals, after preparation, were mounted so that they could be cleaned by ion bombardment, heated by electron bombardment, or illuminated by a monochromatic beam of ultraviolet light while under high vacuum conditions.

### 1. Vacuum System

A diagram of the vacuum system also showing the crystal mount, the ion and electron bombarding arrangement, and the collector is shown in Fig. 1. The vacuum system utilized a mechanical fore pump, three stage oil diffusion pump, Vac-ion pump, molybdenum getters, and cold traps. Gasses were admitted to the system by means of a controlled leak which consisted of a metal vacuum valve between the gas flask and the experimental tube. The diffusion pump was separated from the experimental tube and fore pump by cold traps. Initial pumping was with the fore pump, and after a reasonable pressure was obtained in the fore volume, the diffusion pump was turned on and a mixture of dry ice and acetone placed on the traps. The experimental tube, ionization gauge, and getter tube were baked at about  $300^\circ\text{C}$  for several hours during which time the tubulation external to the oven was heated with an oxygen-gas flame. After baking, the trap between the diffusion pump and the main system was lowered to allow exhaustion of condensable vapors.

If the tube had been open for more than a few days prior to a pump down the getters and filaments were activated at this time. After several hours more of baking the dry ice and acetone trap between the diffusion pump and the experimental tube was replaced by a liquid nitrogen trap. The ionization gauge, a Westinghouse WL 5966, and the bombarding filaments were then outgassed, and the getters activated. Measured pressures of better than  $1 \times 10^{-9}$  mm of Hg were obtained using this method. An indirect method of determining the active gas partial pressure indicated that the latter was less than  $1 \times 10^{-10}$  mm of Hg.

## 2. Heating the Crystal

The crystal was heated by electron bombardment from shielded filaments arranged so that the crystal could be bombarded from the sides. The temperature of the crystal during heating was measured with an optical pyrometer. The pyrometer readings were corrected using an emissivity value of 0.37<sup>15</sup> and adding an additional 15°C to account for the effect of observation through the Pyrex walls.

## 3. Ion Bombardment of the Crystal

Argon for bombardment was admitted to the system through the freshly activated getter tube at a pressure in the range of  $1-10 \times 10^{-3}$  mm of Hg. One of the ion bombarding filaments was heated and several hundred volts applied between the two filaments. The discharge, using 500 ev ions was set up between the collector and the crystal. During bombardment the crystal was positioned so there was no direct path for sputtered material from the filaments to the crystal. After the initial discharge, the bombarding current was maintained at 0.20 ma/cm<sup>2</sup> by varying the gas pressure and the ionizing current.

## 4. Photoelectric Measurements

The collector cylinder mounted axially along the tube was fitted with a door which could be opened to allow the crystal to be moved into the region within the cylinder, where the monochromatic beam could be directed or closed when ion bombardment or heating was being carried out thus preventing sputtered or evaporated material from falling on the quartz window. The photocurrent, collected at 22 vdc, was measured with a Cary Model 31 vibrating reed electrometer.

The ultraviolet source consisted of a Bausch & Lomb grating monochromator (600 lines/mm) the beam from which was directed through the quartz window onto the crystal face by reflection from a front

silvered mirror. The beam focused at the crystal face was about 2 x 8 mm. Fig. 2 shows the essential elements of the collector circuit and the optical system.

The optical system was adjusted prior to the experiment and after these initial settings of slit width, slit height, and lamp position, the only adjustments made with the monochromator were to turn it on at least one-half hour prior to any measurements and to make adjustments in the position of the beam with the external mirror. The photocurrent was measured for the various lines of the mercury spectrum above the threshold frequency. The relative photoelectric yield of the lines was determined by dividing the measured photocurrent by relative intensity values (the total energy of the beam) for the various frequencies. Relative intensity measurements were made with a Golay detector.<sup>16,\*</sup> The Golay detector measures the total energy of the beam directly. These measurements were later checked using an ultraviolet phosphor and photomultiplier tube.<sup>17</sup> The beam from the monochromator was directed onto the phosphor which in turn emits a blue line, the number of photons emitted by the phosphor being proportional to the number of photons incident from the monochromator. The phosphor is linear over the range of wavelength of interest and the amplification of the photomultiplier is constant for sufficiently low level signals so that the current in the last stage of the photomultiplier is proportional to the number of photons incident on the phosphor. With the appropriate correction for wavelength, relative intensity measurements could be made. These measurements of relative intensity were found in good agreement with measurements taken with the Golay detector.

#### 5. Mounting

The crystals were mounted by simply screwing them onto a molybdenum rod. This rod had been outgassed in another vacuum system for several hours at 1400°C prior to assembly. A diagram of the mounting arrangement is shown in Fig. 3.

#### 6. Crystal Preparation

The crystals used in this experiment were cut from single crystals in a large sample of multicrystal material obtained from the DuPont Chemical Company. The orientation of the (111), (110), and (335) faces as determined by x-ray back reflection photographs was good to within two degrees of the desired orientations. The final polishing, after preliminary grinding and polishing with standard metallographic polishes, consisted in alternate polishes with "Shamva" on wax and electropolishing. The electropolish was carried out at

\* These measurements were made at the Eppley Laboratories in Newport, Rhode Island.

about 20 volts with a platinum cathode in a solution of 17-parts sulphuric acid and 3-parts hydrofluoric acid. Polishing times were less than a minute with a current density of about 20 ma/cm<sup>2</sup>. After this treatment the crystals were placed in hot distilled water for several minutes.

### III. Results and Discussion

#### 1. Cleaning Procedure

The technique of ion bombardment and annealing successfully applied to other high temperature materials was used to produce clean surfaces of niobium.<sup>18</sup> Since this cleaning technique had not previously been applied to niobium it was necessary to determine the optimum bombardment time and heating time and temperature.

Initial cleaning of the first crystal (the (111) orientation) started with a 15 minute bombardment.<sup>2</sup> Then the crystal was outgassed by heating for in excess of 100 hours. During this initial outgassing it was necessary to start heating at a very low temperature, about 100°C, otherwise the amount of gas evolved was sufficient to cause large pressure increases. The temperature during the 100 hours of outgassing was slowly raised to 900°C after which very little more gas was evolved. After reaching 900°C the temperature was increased within about 1 hour to 1400°C without appreciable evolution of gas. Since it was assumed that the evolution of gas was accompanied by the diffusion of contaminants from the bulk to the surface, ion bombardments were introduced at roughly 20 hour intervals during the outgassing.

After the crystal had been thoroughly outgassed it was possible to determine the temperature at which the damage introduced by the ion bombardment could be annealed out; this temperature turned out to be 900°C.

Several cycles of ion bombardment and annealing were necessary before the photoelectric data gave consistent work function values and a good fit to the Fowler curve. This was probably due to continued diffusion of contamination from the bulk to the surface.

A preliminary attempt to study the adsorption of oxygen on this crystal presented some very interesting problems that influenced the cleaning procedure. A very rough estimate of the sticking coefficient for oxygen indicated that the value was not very far from unity. The sticking coefficient is defined as the ratio of the number of atoms that strike a surface and stick to the number that strike. Attempts to rejuvenate the surface after oxygen exposure by heating were unsuccessful. Heating the oxygen covered surface for  $\frac{1}{2}$  hour completely eliminated the photoemission. Two cycles of a 30 minute bombardment followed by a  $\frac{1}{2}$  hour heating were needed to restore any emission and several more cycles of shorter bombardments and heatings to restore the original work function

values and a good fit of the Fowler curve. Apparently the oxygen, with heating, does not completely evaporate but at least some diffuses into the crystal.

Further studies of the effect of the annealing time and temperature showed that the work function values, the fit of the Fowler curve, and oxygen adsorption characteristics were independent of the annealing temperature over the range from 900°C to 1400°C and of the annealing time from 15 minutes to 2 hours. Whether the crystal was allowed to radiation cool from its annealing temperature or was brought down slowly over a  $\frac{1}{2}$  hour period did not influence the results.

These preliminary results were used to establish a cleaning procedure for the remainder of the experiment. The standard cleaning cycle consisted of a 15 minute 500 ev argon-ion bombardment at 0.20 ma/cm<sup>2</sup> and an annealing for  $\frac{1}{2}$  hour at 1000°C. The higher value of bombarding current was chosen because of the fear of contamination from oxygen or other active gases. A short annealing time was chosen to minimize the time between the preparation of the clean surface and the oxygen adsorption or work function measurement. If the surface was exposed to oxygen, 2 cleaning cycles were found necessary to completely restore the clean surface. An oxygen covered surface was never heated.

## 2. Work Function Measurements

Work function measurements were made by the Fowler photoelectric technique. In the measurement of work functions and in adsorption studies it is the photoelectric effect near the threshold which is of interest and the Fowler theory not only gives a theoretical description of the phenomenon of photoemission near the threshold but allows presentation of the photoelectric data in a convenient form for determining the work function.<sup>19</sup> The Fowler theory takes account of the variation with temperature of the energy distribution of electrons near the energy maximum so that the true threshold (the threshold at absolute zero of temperature) and work function can be measured at any temperature. The essential problem to which the Fowler theory is addressed is that of calculating the number of electrons ejected from a surface at a temperature  $T$  by radiation of frequency  $\nu$  which is close to  $\nu_0$ .<sup>20</sup> The result of the Fowler theory is an expression for the photoelectric current density; this expression written in a convenient form for plotting is

$$\log (I/T^2) = D + F(y)$$

where  $I$  is the photoelectric current density (photoelectric yield per unit light intensity),  $T$  is the absolute temperature,  $D$  is a constant, and  $F(y)$  is a universal function which is the same for all metals and for all temperatures. A graph of  $F(y) = \log (I/T^2) - D$  versus  $y = h(\nu - \nu_0)/kT$  is the Fowler curve. (The Fowler curve is shown in Fig. 4.).

Now, if the observed values of the photoelectric yield are plotted in the form  $\log(I/T^2)$  as a function of  $h\nu/kT$  then this curve, if shifted horizontally by an amount  $h\nu_0/kT$  and vertically by an amount  $D$ , should coincide with the theoretical curve. The amount of horizontal shift is a measure of the work function. The values of the work functions of the three planes as determined by fitting a plot of  $\log(I/T^2)$  versus  $h\nu/kT$  to the Fowler curve are: (111), 4.66 ev; (110), 4.33 ev; (335), 4.55 ev. These values are the average of 5 or more values for each plane; the error is  $\pm 0.02$  ev.

The fact that the (111) plane has a higher work function than that of the (110) plane differs from the results previously reported for tungsten.<sup>21,22</sup> For tungsten, which has the same structure (body-centered-cubic), as niobium, the (110) plane had the higher work function. Although the work function of niobium has not been measured in the field emission microscope, field electron microscope patterns from niobium indicate that like tungsten and molybdenum the (110) plane is a high work function plane.<sup>23</sup> The orientations of our samples after removal from the system were checked again to assure that no recrystallization had taken place so that it is felt that the values quoted here are the correct ones for these faces.

A typical plot of the photoelectric data fitted to the Fowler curve is shown in Fig. 4. The values of  $I$  are found by dividing the photocurrent for a particular spectrum line by the relative intensity (relative to the other lines) of that line. The points on the curve are found by plotting  $\log(I/T^2)$  for each of the lines of the spectrum as a function of the values of  $h\nu/kT$  for the various lines. The work function is  $kT$  times the value of  $h\nu/kT$  which coincides with zero on the Fowler curve. The data shown in Fig. 4 are from the (335) plane. The work function on ion bombarded surfaces of all planes was the same, 4.09 ev. This value is the average of more than 12 different values, 4 from each plane. The error is  $\pm 0.02$  ev.

### 3. Oxygen Adsorption on Clean Surfaces

The effect of room temperature oxygen adsorption on the clean surfaces of all three faces was the same and resulted in work function increases of several tenths of an ev. The sticking coefficient for oxygen was found to be 0.9. There are two problems encountered in attempting to measure the sticking coefficient. First, there is the problem of measuring the amount of exposure to a particular adsorbate,

and second, there is the problem of determining when a monolayer of coverage has been achieved. In the case of oxygen, the ionization gauge not only does not measure the true pressure of oxygen but converts some of the oxygen to carbon monoxide.<sup>24</sup> Appropriate corrections to the gauge readings were made to determine the actual oxygen pressure (gauge reading was multiplied by 2.5).<sup>14</sup> The effects of the formation of carbon monoxide were minimized by making the exposures dynamically, that is the system was continuously pumped during an exposure. Later tests on the (335) face indicated that the sticking coefficient for carbon monoxide was at least an order of magnitude lower than that of oxygen.

The variation of the work function with oxygen exposure was determined in the following way. The decay of several strong spectral lines was monitored as a function of the exposure. The relative strength of these lines plotted as a function of exposure is shown in Fig. 5. It was necessary to do several exposures, monitoring one or two lines at a time, to plot a graph such as Fig. 5. There was considerable variation in the amount of exposure needed to produce the decay curve characteristic of a particular line; however, the shape of the decay curve characteristic of that line and its position with respect to the other lines was always the same. This variation is no doubt due to the errors encountered in measuring the oxygen pressure with an ionization gauge. The curves of Fig. 5 were drawn after many exposures. Exposures on the other planes produced curves identical to those shown in Fig. 5 within the limits of the error in measuring the oxygen pressure. Knowing the relative beam strengths at the various exposures plots of  $\log(I/T^2)$  versus  $h\nu/kT$  could be constructed, compared with the Fowler curve to determine the work function, and the work function then plotted as a function of the exposure. The practical limitation of this procedure is that as the work function increases the longer wavelength lines go out and there are fewer points for the  $\log(I/T^2)$  versus  $h\nu/kT$  curves. These curves constructed from the decay curves fit the Fowler curve quite well considering that at an exposure of  $5 \times 10^{-8}$  mm Hg min there are only three points with which to draw the curve. In Fig. 6 the work function is plotted as a function of the oxygen exposure for all three planes.

The sticking coefficient was calculated assuming that an exposure of  $10^{-7}$  mm Hg min amounts to a monolayer of coverage. This value was selected because the two lowest wavelength lines, and to a lesser extent the other two lines, appear to be heading toward this value on the exposure axis. The ratio of the number of niobium atoms per  $\text{cm}^2$  available as adsorption sites to the number of oxygen molecules that would strike a  $\text{cm}^2$  in an exposure of  $10^{-7}$  mm Hg min is taken as the sticking coefficient. These values of sticking coefficient are not necessarily comparable to sticking coefficients measured by other methods. The ionization gauge not only is inaccurate as a pressure measuring instrument in the pressure range necessary for these measurements but is an active element in the system. These measurements of sticking coefficient can however be compared to the work on silicon and germanium in which the sticking coefficients were measured in roughly the same manner.<sup>13,14</sup> The very high values of sticking coefficient found here certainly suggest that the surface must have been quite clean to start with. The fact that the sticking coefficient for CO was much less than that for oxygen also suggests that the CO generated by the ionization gauge filament did not substantially influence the oxygen adsorption measurement.

The very high sticking coefficient for oxygen on niobium makes this an ideal material with which to make an indirect measurement of the partial pressures of active gases residual in the vacuum system. After preparing a clean surface the decay of the photocurrent for the various lines of the spectrum is monitored over a period of several days. The decay of the various lines is plotted as a function of time and compared with curves of the decay of these same lines with known oxygen exposures. The pressure that would make these curves coincide is taken as the active gas partial pressure. Active gas partial pressures estimated in this way were in the  $10^{-11}$  mm Hg range. The fact that liberal use is made of molybdenum getters which are known to reduce the partial pressure of oxygen suggests that the principal component of the residual gas is carbon monoxide.

#### 4. Oxygen Adsorption on Ion Bombarded Surfaces

Oxygen adsorption on ion bombarded surfaces (not annealed) resulted in work function increases of a few tenths of an ev. The sticking coefficient for oxygen was found to be 0.2. As was found on the clean surfaces, the effect of oxygen adsorption was to reduce the beams in the same manner on all three faces. The relative strength of the various lines plotted as a function of exposure is shown in Fig. 7. On the ion bombarded surfaces the beams all decayed at about the same rate whereas on the clean surfaces the longer wavelength lines decayed at higher rates. The variation of the work function with oxygen adsorption was determined in the manner previously described. The work function as a function of oxygen exposure is shown in Fig. 8.



## 5. Effect of Ion Bombardment on Work Function

The work function of ion bombarded but not annealed surfaces was found to depend on the extent of the bombardment for bombardments of less than one minute carried out at  $0.20 \text{ ma/cm}^2$ . A study of the effect of the extent of bombardment on the work function of the (335) plane of niobium indicated that for a very short bombardment of 20 seconds at  $0.20 \text{ ma/cm}^2$  the work function was about 4.7 ev (the clean value was 4.55 ev.). The variation of the work function with extent of bombardment for the (335) face is shown in Fig. 9. A bombardment of  $100 \text{ amp/cm}^2$  for 1 second removes about 1 atomic layer. These bombardments were all carried out on clean, annealed surfaces. Short bombardments (of less than 1 minute) carried out on (a) surfaces which had previously been given a long ion bombardment, (b) clean, annealed surfaces or (c) clean surfaces that have been subjected to a very short bombardment always give work function values higher than the original ones. Many short bombardments one after the other do not result in a work function characteristic of the long ion bombardment even though the total bombardment may amount to several minutes. A bombardment carried out for one minute is not equivalent to say ten bombardments each carried out for one-tenth of a minute.

## 6. Ion-bombardment Etching

In Figs. 10-12 are shown optical photographs of the surfaces of the (111), (110), and (335) planes after chemical preparation and after ion-bombardment etching.

The "A" photographs were taken after the chemical preparation previously described. The (111) surface exhibits a number of the ring-like patterns. Both the (110) and the (335) surfaces exhibited a very grainy appearance after chemical preparation.

The "B" photographs were taken after an total ion bombardment for 500 minutes at  $0.20 \text{ ma/cm}^2$  with 500 ev argon ions. The effect of this bombardment was to produce a small number of etch pits which were circular on the (111) face, oval on the (110) face and triangular on the (335) face. These patterns are similar to those previously observed on silicon and germanium.<sup>25</sup> The ring-like patterns observed on the (111) face after chemical preparation were not disturbed by the bombardment. These patterns which have been observed only on the (111) plane are much too large to be explained by the existence of screw-type dislocations. They seem to be the result of the electrolytic etching process, and further work is in progress to determine their exact cause.

## IV. Summary

The values of the work function for the three planes of niobium single crystals prepared in high vacuum by the ion bombardment cleaning process are in the order (111), (335), and (110). High-temperature

heating of oxygen covered surfaces was found not to produce clean surfaces, and it was necessary to use the ion bombardment and annealing method of cleaning to produce clean surfaces. The work function of the ion bombarded surfaces of all of the planes was the same.

The sticking coefficient for oxygen was found to be the same for clean surfaces of all three planes. On the ion bombarded surfaces (all three planes) the sticking coefficient was of a lower value than on the clean surface. The manner of oxygen adsorption on the clean surfaces was the same and resulted in identical increases in the work function for each crystalline orientation. The manner of oxygen adsorption on the ion bombarded surfaces was also independent of the face and resulted in an increase in the work function.

The work function of ion bombarded surfaces was also shown to be dependent on the extent of bombardment for very short bombardments and that generally shorter bombardments resulted in higher work functions. This effect has not previously been reported. The increase in work function for short bombardments occurs when the bombardments result in the removal of less than 100 atomic layers.

In the ion bombardment and annealing cleaning technique, the ion bombardments employed result in the removal of more than 1000 atomic layers. There have been many cases, particularly in adsorption studies with microbalances, where surfaces have been prepared by ion bombardment alone. In some of these experiments, the bombardment resulted in the removal of between 10 and 100 atomic layers.<sup>11,12</sup> Surfaces prepared by these very short bombardments are not equivalent to those prepared using the longer bombardments, and the present work shows that in this region the surface is undergoing a rather rapid change with extent of bombardment. Thus, the work done on surfaces prepared by these very short bombardments is not necessarily comparable with work done on the more heavily bombarded surfaces.

A possible explanation of this increase in work function with very short bombardments is that the surface is becoming contaminated with oxygen or other active gases during the initial stages of the bombardment and that this contamination is removed only when the bombardment has reached a sufficiently large value. This argument does not seem applicable, however, for several reasons. First, the sticking coefficient for oxygen on surfaces subjected to these short bombardments though not investigated in detail was found to be somewhere between the values for the ion bombarded and the clean surfaces (0.2 and 0.9 respectively). This high value of sticking coefficient itself is indicative of a clean surface. Second, the photoelectric yield decreases drastically with known oxygen adsorption as shown in Figs. 5 and 7. The yield was

generally lower for the lightly bombarded surfaces but the effect was no where near as pronounced as for the case of known oxygen adsorption. Third, a bombardment of 10 thousand microampere-seconds/cm<sup>2</sup> amounts to around  $10^{18}$  ions and to obtain a monolayer of contamination one in  $10^4$  atoms would have to be an active impurity. The purity of the argon is better than one part of  $10^5$  even before it is passed through the active getter. Fourth, attempts to contaminate surfaces (either ion bombarded or clean surfaces) by exposing them to argon for exposures of  $10^{-2}$  mm Hg min resulted in no work function increases. This indicated that the amount of active gases in the argon is negligibly small. For these four reasons, it does not seem that the observation can be explained on the basis of inadvertent contamination of the sample during bombardment.

One of the original theories of the sputtering process was that the impinging ions produced sufficient local heating to remove surface atoms by evaporation. This theory has since been disproved, primarily by the observation that the atoms are ejected in preferential directions. The fact that the ion bombardment process does not appear to reach some type of equilibrium condition until the removal of about 100 atomic layers suggests that the effect of the first few ions is quite different from that produced after equilibrium has been reached. This pseudo equilibrium may be the result of a temperature gradient in the sample which is produced by some of the energy of the ions going into thermal vibrations of the atoms, particularly those near the surface. It may be that thermal equilibrium is reached only after the bombardment has continued for some time.

This observation that at least one physical property, namely, the work function, depends on the extent of ion bombardment should lead to further work to determine the effect of the extent of bombardment on other physical properties and to a study of the types of defects introduced by the bombardment process.

It must be kept in mind that this work concerning the dependence of work function on the extent of ion bombardment was carried out on a high index plane. The effect may be different on a less complex plane and similar studies must be undertaken on low index planes.

REFERENCES

1. H. B. Michaelson, J. Appl. Phys. 21, 536 (1950).
2. C. Herring, and M. H. Nichols, Revs. Mod. Phys. 21, 185 (1949).
3. H. B. Wahlen and L. L. Sordahl, Phys. Rev. 45, 886 (1934).
4. A. L. Reimann and C. K. Grant, Phil. Mag. 22, 34 (1936).
5. J. A. Dillon, Jr., and R. M. Oman, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Publishing House of the Czechoslovak Academy of Sciences, Prague, 1961), p. 533.
6. Allen, Eisinger, Hagstrum, and Law, J. Appl. Phys. 30, 1563 (1959).
7. Allen, Buck, and Law, J. Appl. Phys. 31, 979 (1960).
8. C. A. Hampel, Rare Metals Handbook (Reinhold Publishing Corp., Chapman & Hall, Ltd., London, 1961), p. 149.
9. G. L. Miller, Tantalum and Niobium (Academic Press, New York, 1959).
10. S. Wagener, J. Phys. Chem. 61, 267 (1957).
11. D. Shooter, Vacuum Microbalance Techniques, (Plenum Press, 1963). Vol. 3.
12. S. P. Wolsky and E. J. Zdanuk, Sixth National Symposium on Vacuum Technology (Pergamon Press, New York, 1960), p. 6.
13. J. A. Dillon, Jr., and H. E. Farnsworth, J. Appl. Phys. 28, 174 (1957).
14. J. A. Dillon, Jr., and H. E. Farnsworth, J. Appl. Phys. 29, 1195 (1958).
15. G. L. Miller, Tantalum and Niobium (Academic Press, New York, 1959), p. 370.
16. M. J. E. Golay, Rev. Sci. Instr. 18, 347 (1947); 20, 816 (1949).
17. A. M. Smith, Investigations of Photoconductivity and Photoemission in Lead Sulfide in the Vacuum Ultraviolet, Thesis, University of Rochester (1961).

REFERENCES (Continued)

18. Farnsworth, Schlier, George, and Burger, J. Appl. Phys. 29, 1150 (1958).
19. R. H. Fowler, Phys. Rev. 38, 45 (1931).
20. A. L. Hughes and L. A. DuBridge, Photoelectric Phenomena (McGraw-Hill Book Co., Inc., New York, 1932).
21. R. Smoluchowski, Phys. Rev. 60, 661 (1941).
22. M. H. Nichols, Phys. Rev. 57, 297 (1940).
23. E. W. Müller, private communication.
24. R. E. Schlier, J. Appl. Phys. 29, 1162 (1958).
25. J. A. Dillon, Jr., and R. M. Oman, J. Appl. Phys. 31, 26 (1960).

FIGURE CAPTIONS

- Fig. 1. Schematic diagram of the vacuum system.
- Fig. 2. Schematic diagram of the photoelectric system.
- Fig. 3. Crystal mounting arrangement.
- Fig. 4. A typical plot of the photoelectric data ( $\log(I/T^2)$  versus  $h\nu/kT$ ) fitted to the Fowler curve ( $F(y)$  versus  $y$ ).
- Fig. 5. Relative photocurrent of several spectral lines as a function of oxygen exposure on clean surfaces.
- Fig. 6. Variation of the work function with oxygen exposure on clean surfaces.
- Fig. 7. Relative photocurrent of several spectral lines as a function of oxygen exposure on ion bombarded surfaces.
- Fig. 8. Variation of the work function with oxygen exposure on ion bombarded surfaces.
- Fig. 9. Variation of the work function with the extent of bombardment for the (335) surface. The energy of the ions was 500 ev and the current density 0.20 ma/cm<sup>2</sup>. The work function of the clean surface was 4.55 ev and for the heavily bombarded surface 4.09 ev.
- Fig. 10. The (111) surface: A, after chemical preparation; B, after ion bombardment for 500 minutes at 0.20 ma/cm<sup>2</sup>. Scale length 50 microns.
- Fig. 11. The (110) surface: A, after chemical preparation; B, after ion bombardment for 500 minutes at 0.20 ma/cm<sup>2</sup>. Scale length 50 microns.
- Fig. 12. The (335) surface: A, after chemical preparation; B, after ion bombardment for 500 minutes at 0.20 ma/cm<sup>2</sup>. Scale length 50 microns.

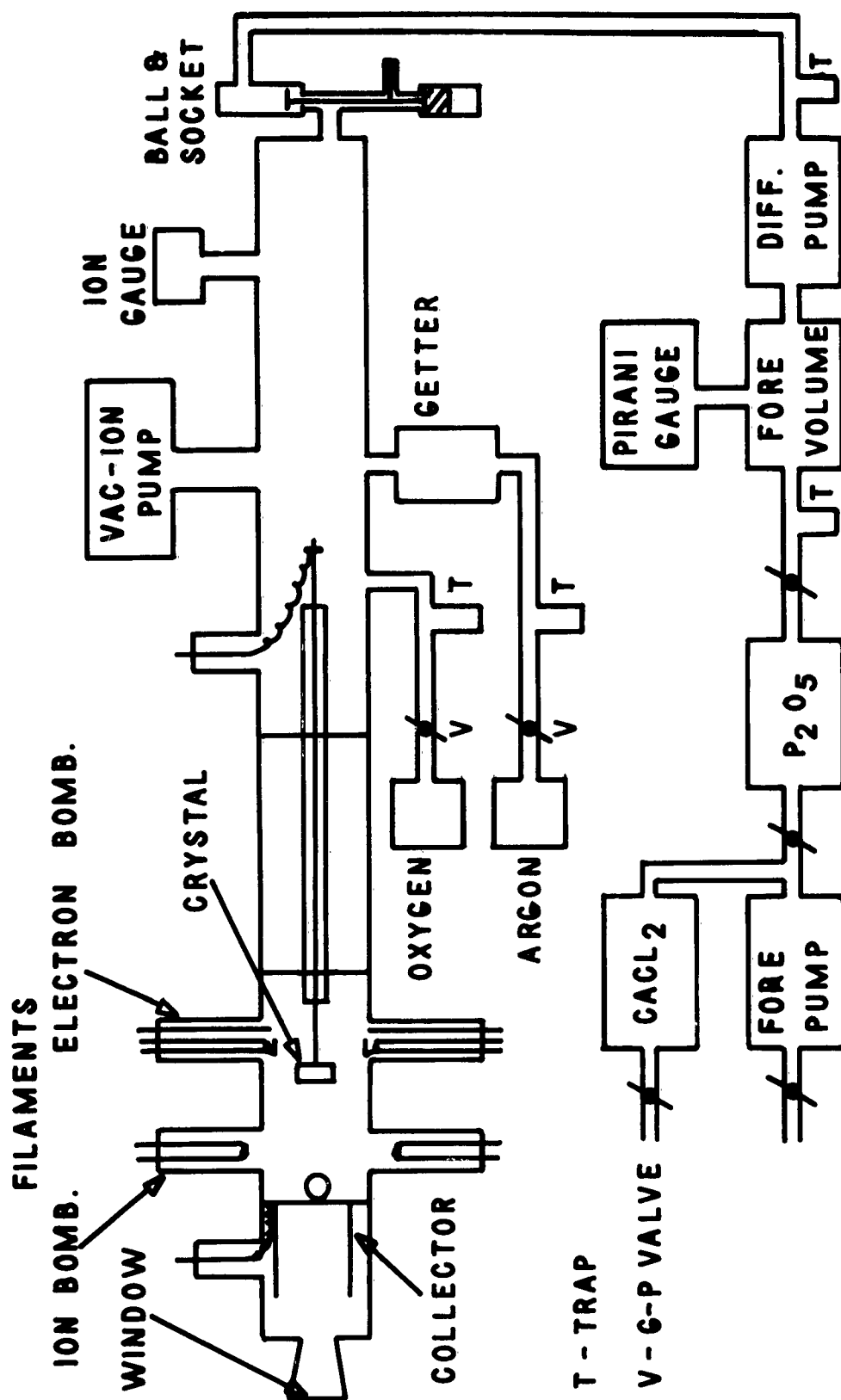


FIG.1

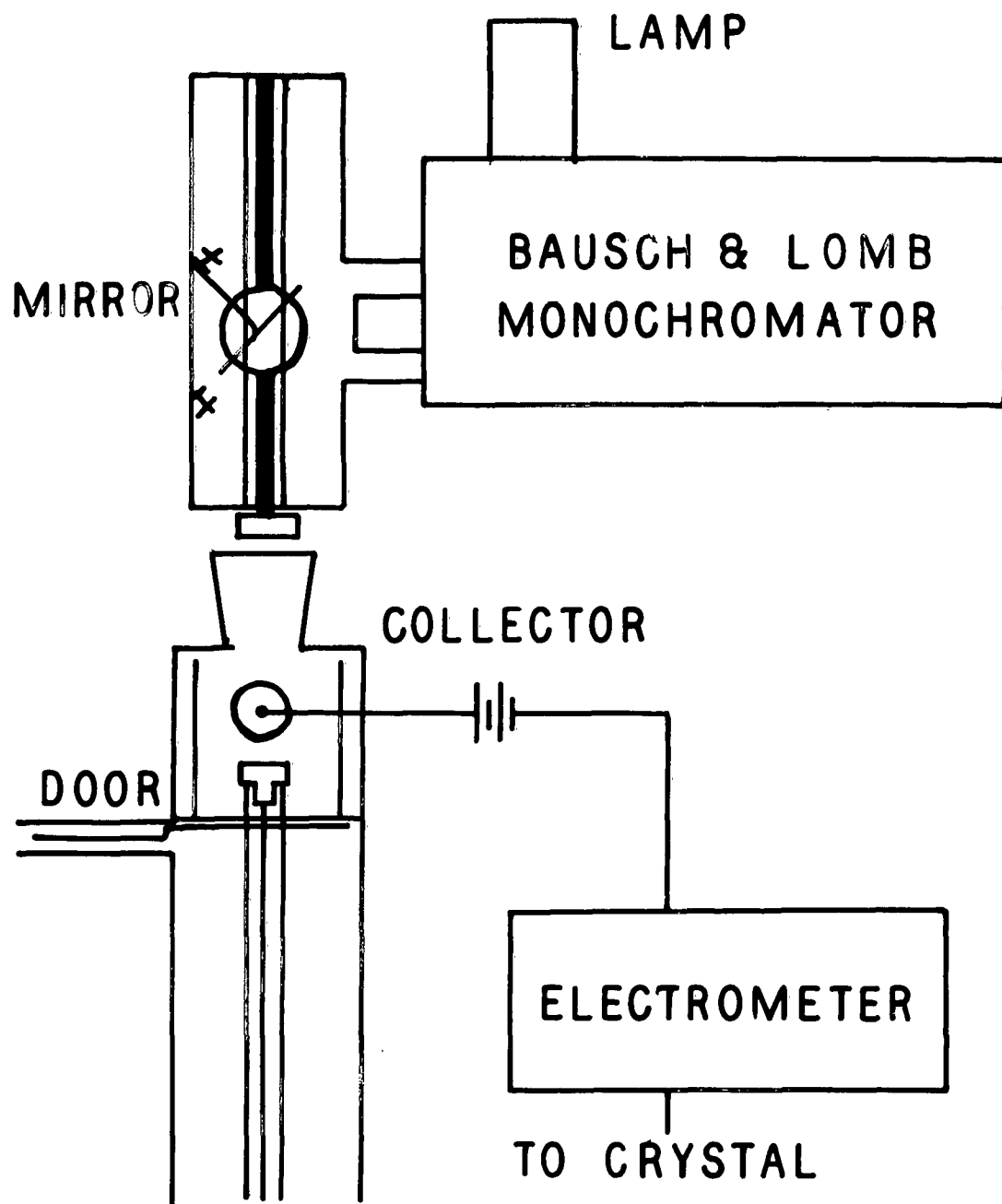


FIG. 2



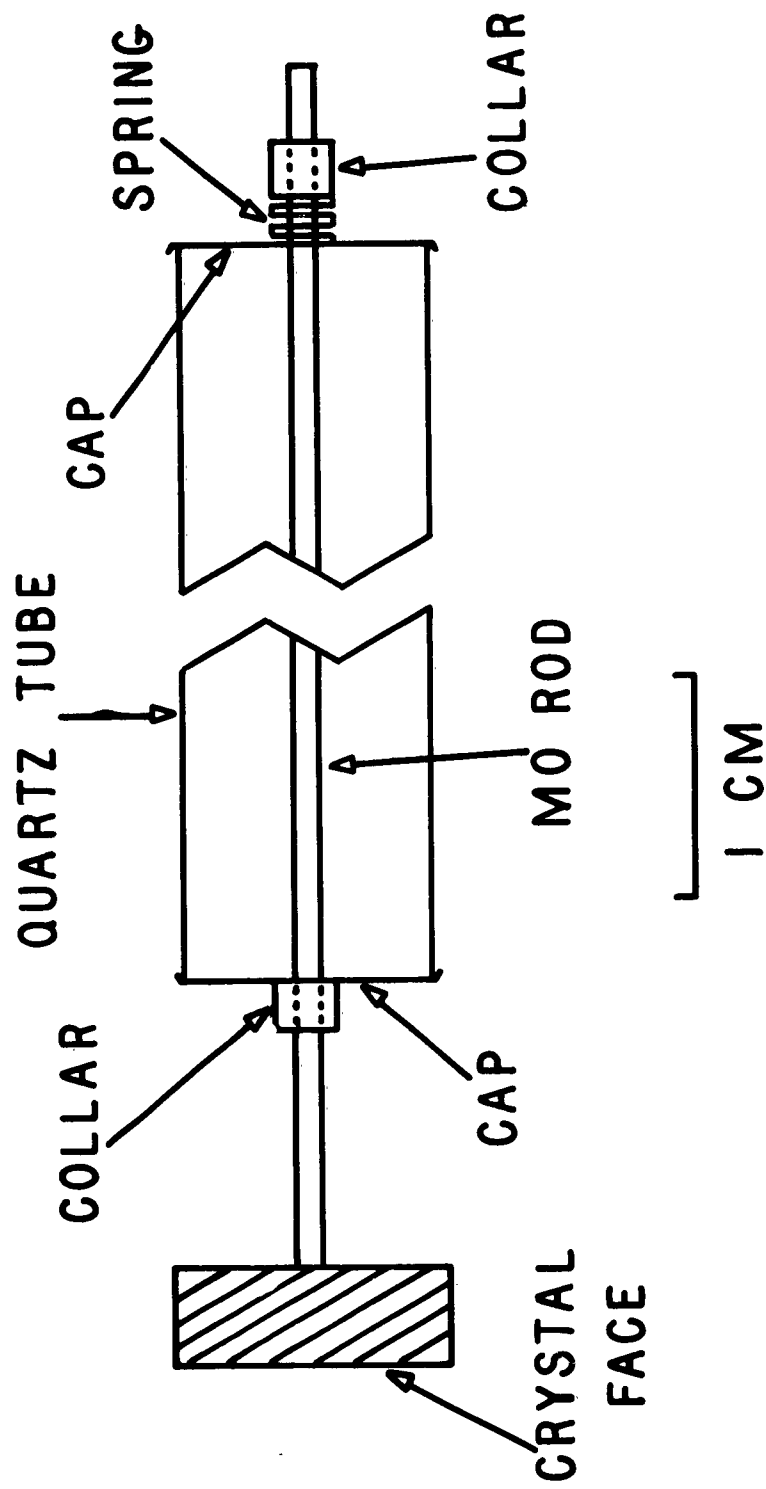


FIG. 3

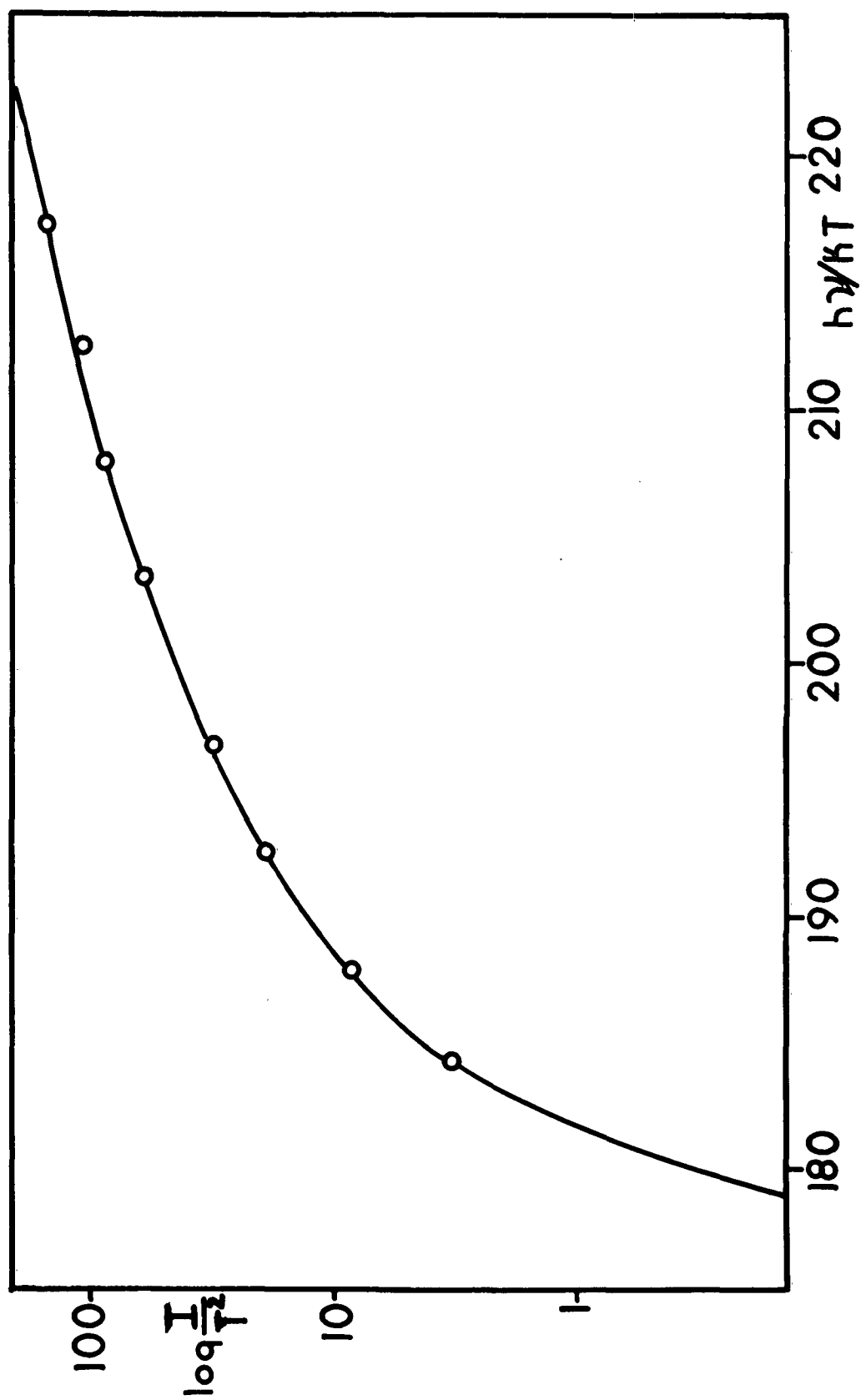


FIG. 4

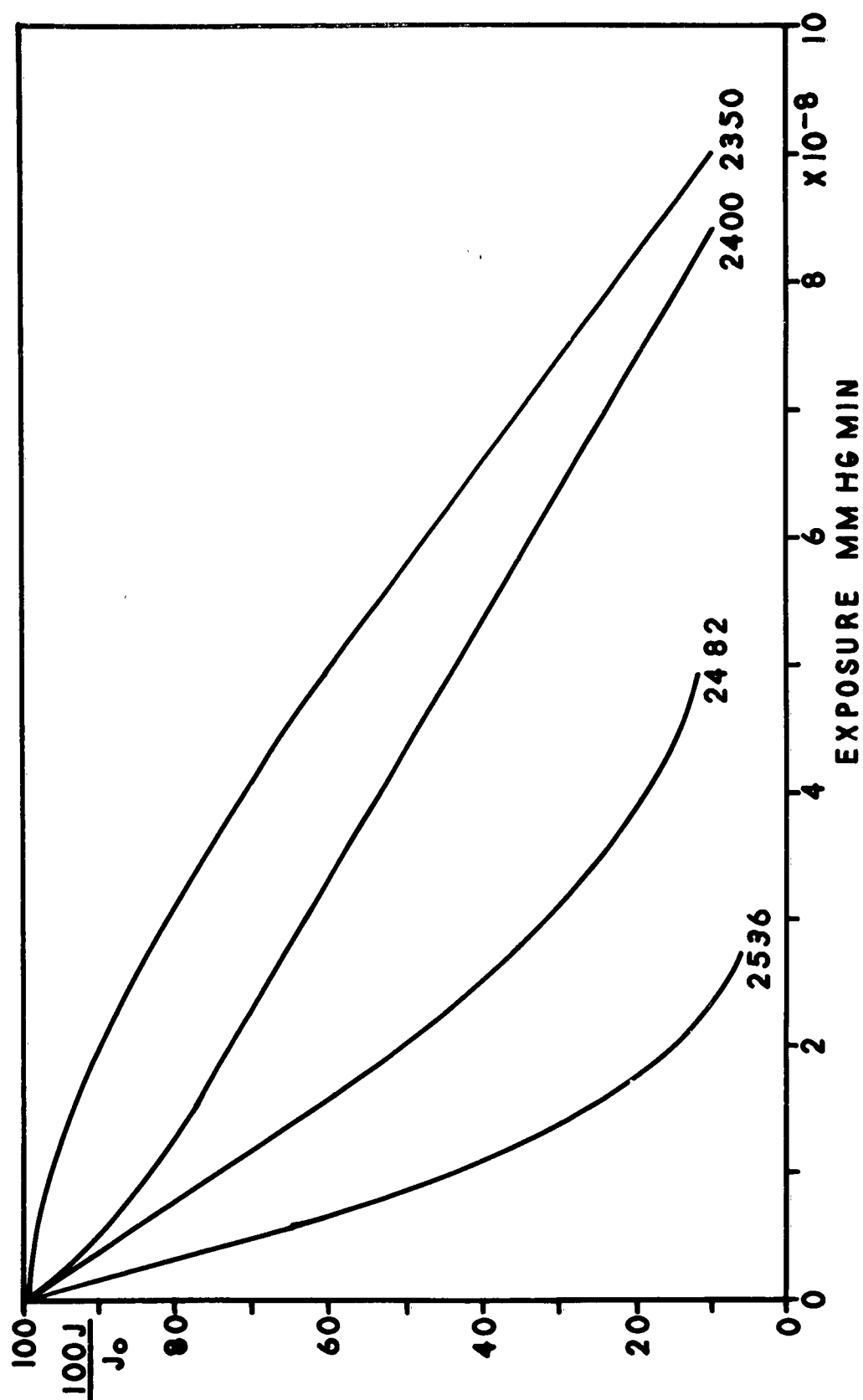


FIG. 5

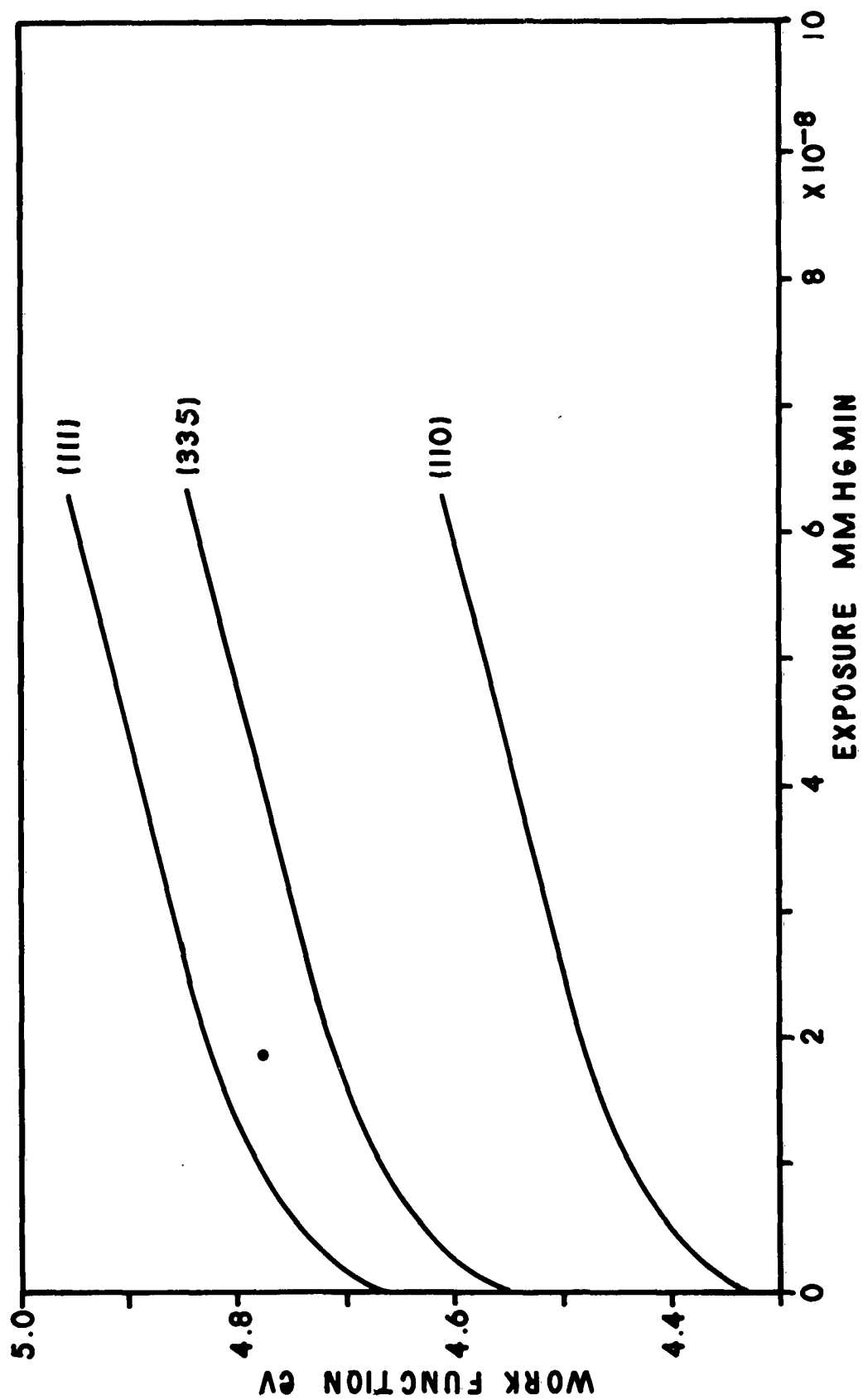


FIG. 6

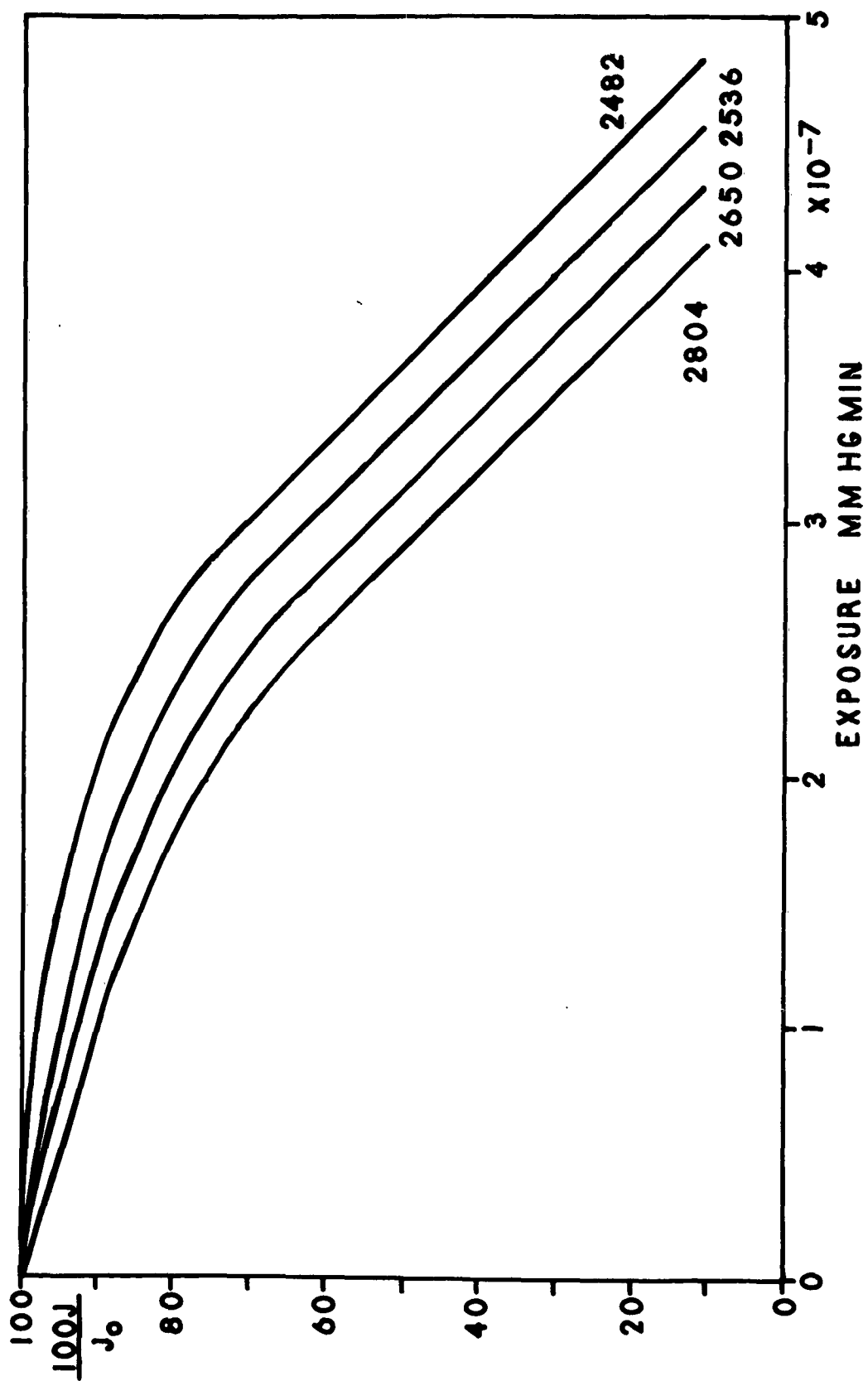


FIG. 7

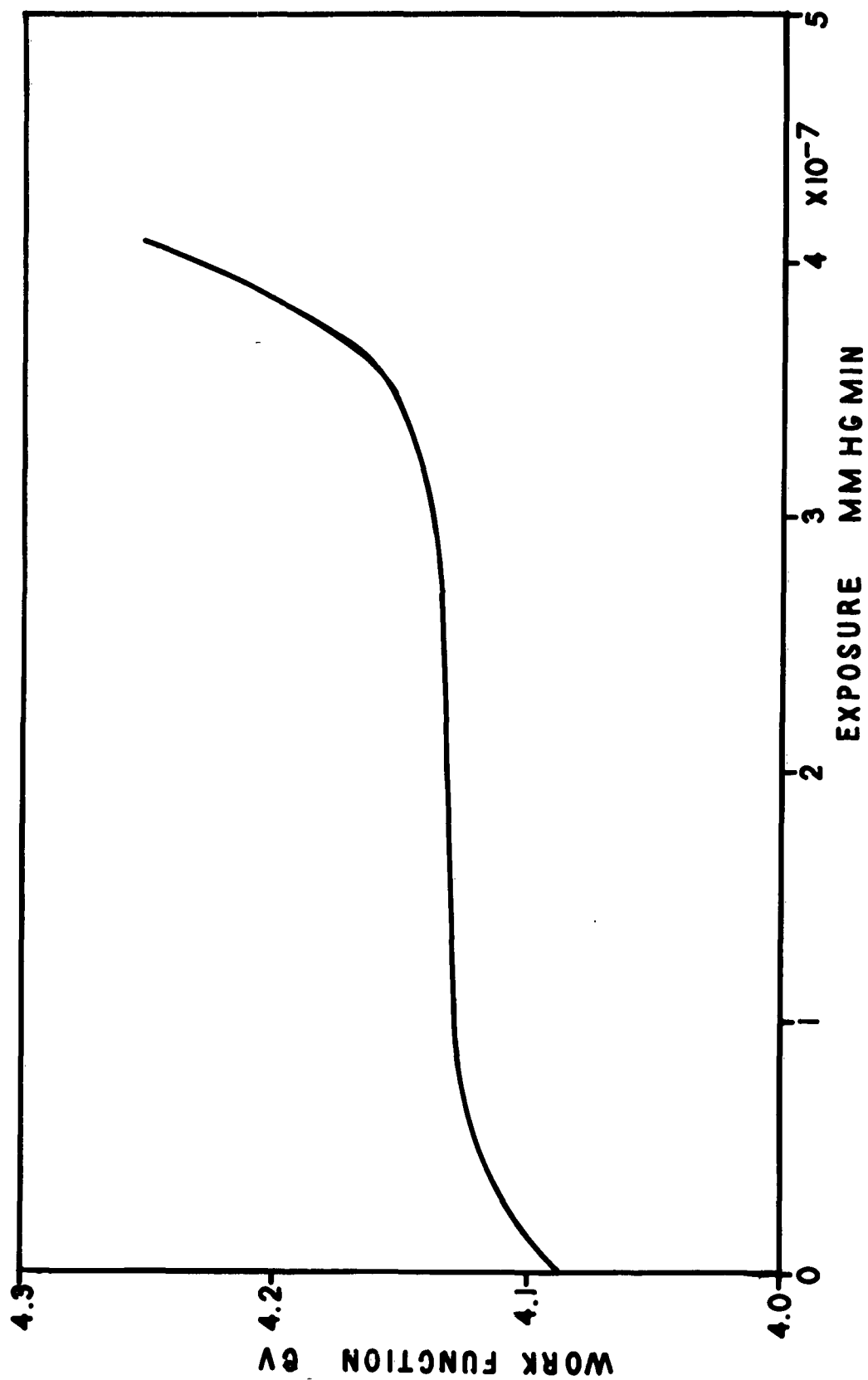


FIG. 8

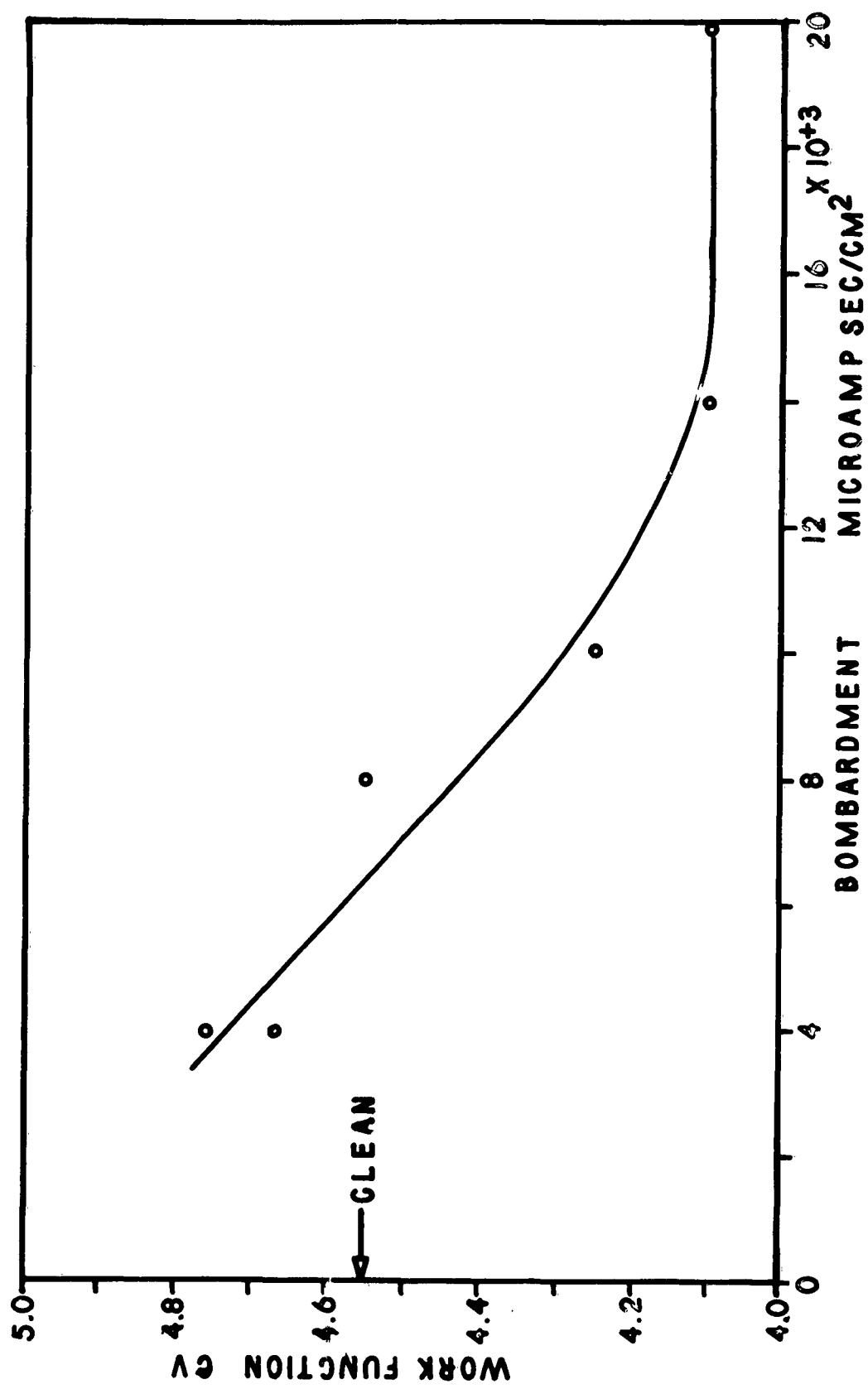
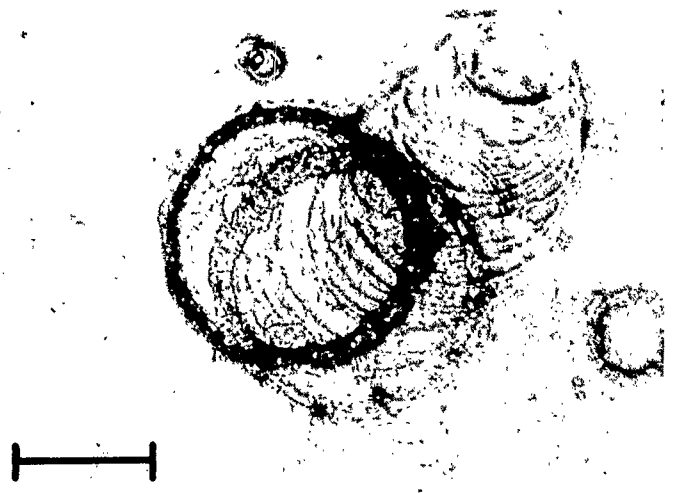


FIG. 9

**A**



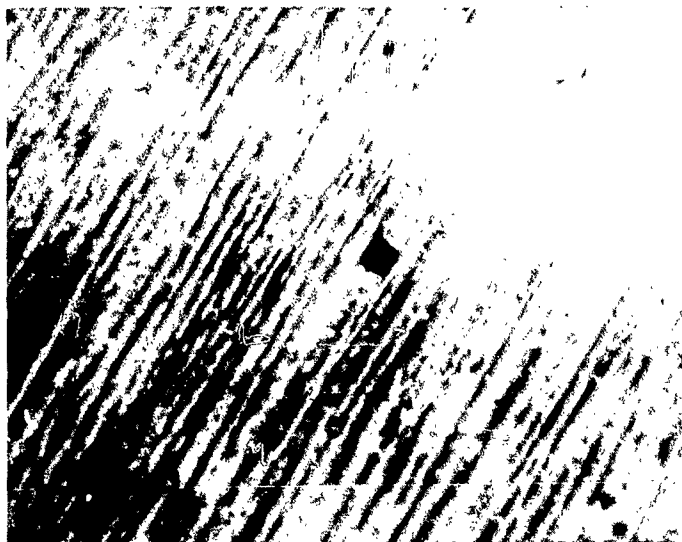
**B**



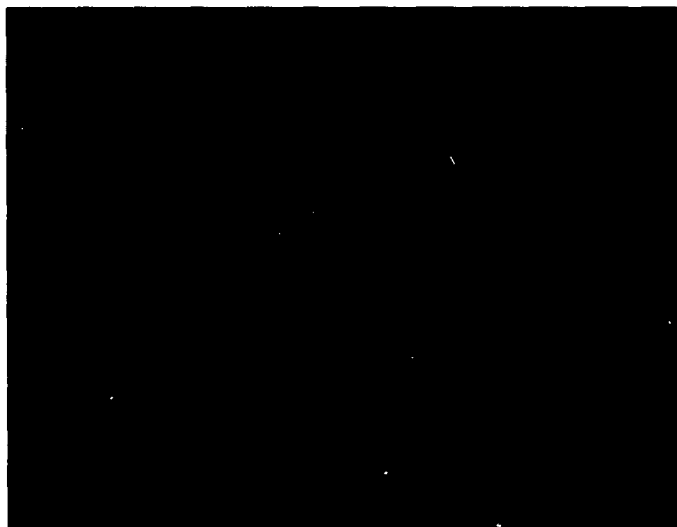
**FIG.10**



**A**

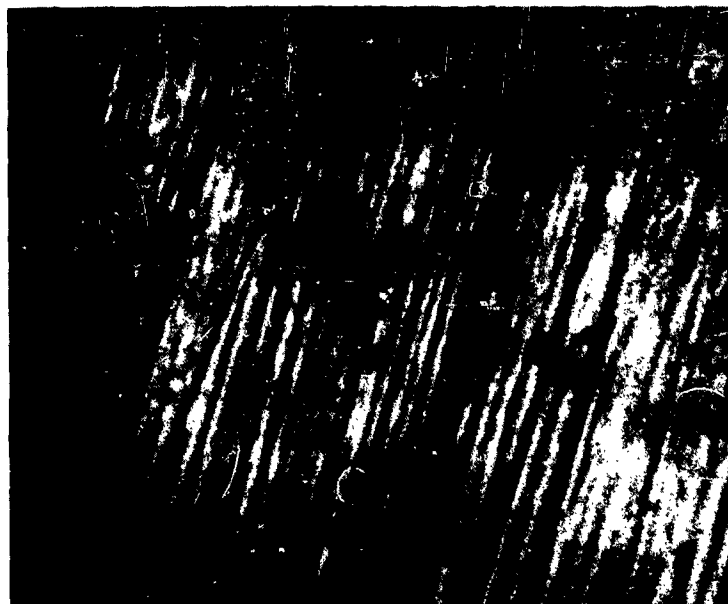


**B**

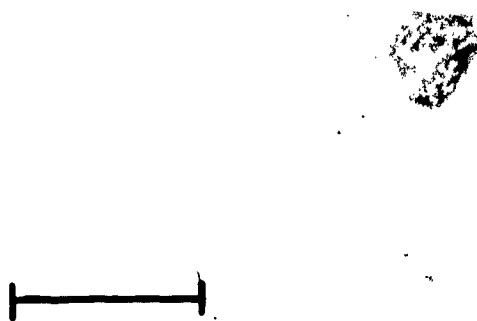


**FIG. 11**

**A**



**B**



**FIG. 12**

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